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### (54) LITHOGRAPHIC PRINTING FORM PRECURSOR AND ITS USE BY HEAT IMAGING

VORLÄUFER EINER LITHOGRAPHISCHEN DRUCKFORM UND IHRE VERWENDUNG BEI DER  
BEBILDERUNG DURCH WÄRME

PRECURSEUR DE PLAQUE D'IMPRESSION LITHOGRAPHIQUE ET SON UTILISATION POUR LA  
GENERATION D' IMAGES PAR LA CHALEUR

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US-A- 5 372 907 US-A- 5 491 046

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## Description

[0001] This invention relates to positive working lithographic printing form precursors, and to their use by methods which involve the delivery of heat.

[0002] The art of lithographic printing is based on the immiscibility of oil and water, wherein the oily material or ink is preferentially retained by the image area and the water or fountain solution is preferentially retained by the non-image area. When a suitably prepared surface is moistened with water and an ink is then applied, the background or non-image area retains the water while the image area accepts ink and repels the water. The ink on the image area is then transferred to the surface of a material upon which the image is to be reproduced, such as paper, cloth and the like.

Commonly ink is transferred to an intermediate material called the blanket which in turn transfers the ink to the surface of the material upon which the image is reproduced.

[0003] A generally used type of lithographic printing form precursor has a light sensitive coating applied to an aluminium base support. Negative working lithographic printing form precursors have a radiation sensitive coating which when imagewise exposed to light hardens in the exposed areas. On development the non-exposed areas of the coated composition are removed leaving the image. On the other hand positive working lithographic printing form precursors have a coated composition, which after imagewise exposure to light of an appropriate wavelength, become more soluble in the exposed areas than in the non-exposed areas in a developer. This light induced solubility differential is called photosolubilisation. A large number of commercially available positive working printing form precursors coated with quinone diazides together with a phenolic resin work by photosolubilisation to produce an image. In both cases the image area on the printing form itself is ink-receptive or oleophilic and the non-image area or background is water receptive or hydrophilic.

[0004] The differentiation between image and non-image areas is made in the exposure process where a film is applied to the printing form precursor with a vacuum to ensure good contact. The printing form precursor is then exposed to a light source, a portion of which is composed of UV radiation. In the instance where a positive printing form precursor is used, the area of the film that corresponds to the image on the printing form precursor is opaque so that no light will strike the printing form precursor, whereas the area on the film that corresponds to the non-image area is clear and permits the transmission of light to the coating which becomes more soluble and is removed.

[0005] More recent developments in the field of lithographic printing form precursors have provided radiation-sensitive compositions useful for the preparation of direct laser addressable printing form precursors. Digital imaging information can be used to image the printing form precursor without the need to utilise an imaging master such as a photographic transparency.

[0006] An example of a positive working, direct laser addressable printing form precursor is described in US 4,708,925, issued November 24th 1987. This patent describes a lithographic printing form precursor in which the imaging layer comprises a phenolic resin and a radiation-sensitive onium salt. As described in the patent, the interaction of the phenolic resin and the onium salt produces an alkali-insoluble composition which is restored to alkali solubility upon photolytic decomposition of the onium salt. The printing form precursor can be utilised as a positive working printing form precursor or as a negative working printing form precursor using additional process steps between exposure and development as detailed in British Patent No. 2,082,339. The printing form precursors described in US 4,708,925 are intrinsically sensitive to UV radiation and can be additionally sensitised to visible and infra-red radiation.

[0007] A further example of a laser addressable printing form precursor which can be utilised as a direct positive working system is described in US 5,372,907, issued December 13th 1994, and US 5,491,046, issued February 13th 1996. These two patents describe a radiation induced decomposition of a latent Bronsted acid to increase the solubility of the resin matrix on imagewise exposure. As with the printing form precursor described in US 4,708,925 these systems can be additionally utilised as a negative working system with additional process steps after imaging and pre-development. In the negative working process the decomposition by-products are subsequently used to catalyse a cross-linking reaction between resins to insolubilise the imaged areas prior to development. As in US 4,708,925 these printing form precursors are intrinsically sensitive to UV radiation due to the acid generator materials used.

[0008] The hereinabove described printing form precursors of the prior art which can be employed as direct imaged positive working printing form precursors are lacking in one or more desirable features. None of the printing form precursors described can be handled extensively without due consideration for the lighting conditions in the working area. In order to handle the printing form precursors for unlimited periods special safelighting conditions are required which prevent unwanted exposure to UV radiation. The printing form precursors may be utilised for limited periods only in white light working conditions dependent upon the output spectrum of the white light source. It would be desirable to utilise digital imaging hardware and printing form precursors in the unrestricted, white light press room environment in order to streamline workflows and UV sensitivity would be a disadvantage in these areas. In addition, white light handling would provide an improved working environment in traditional pre-press areas which currently have to be under restrictive safelighting conditions.

[0009] Moreover, both printing form precursor systems have constraints on their components which create difficulties

in optimising plate properties to provide optimum performance across the wide range of demanding lithographic plate performance parameters, including developer solubility, ink receptivity, runlength, adhesion.

[0010] In the systems described in US 4,708,925 the presence of functional groups which would crosslink the phenolic resin in the presence of the onium salts upon radiation cannot be allowed, either as a modification to the alkali soluble resin or as additional components in the compositions, as this would lead to reduced solubilisation on exposure.

[0011] An essential requirement of the compositions described in US 5,491,046 is the presence of both a resole resin and a novolak resin in order to allow the use of the system in a negative working mode. This is the favoured mode for this system as demonstrated by the negative working patent examples and the first commercialised product derived from the proprietary technology, Kodak's Performer product. This optimisation for negative working potential restricts optimisation for the positive working mode which does not have this requirement.

[0012] A wide range of heat solubilising compositions useful as thermographic recording materials have previously been disclosed in GB 1,245,924, issued September 15th 1971, such that the solubility of any given area of the imagable layer in a given solvent can be increased by the heating of the layer by indirect exposure to a short duration high intensity visible light and/or infrared radiation transmitted or reflected from the background areas of a graphic original located in contact with the recording material. The systems described are varied and operate by many different mechanisms and use different developing materials ranging from water to chlorinated organic solvents. Included in the range of compositions disclosed which are aqueous developable are those which comprise a novolak type phenolic resin. The patent suggests that coated films comprising of such resins will show increased solubility on heating. The compositions may contain heat absorbing compounds such as carbon black or Milori Blue (CI Pigment Blue 27). These materials additionally colour the images for their use as a recording medium.

[0013] The level of solubility differential in the compositions described in GB 1,245,924, however, is very low compared to that of commercial positive working lithographic printing form precursor compositions. Standard lithographic printing form precursors are able to demonstrate excellent tolerance to strong developing solutions, good robustness to variations in customer use and can be optimised to provide high developer solution usage and high numbers of printed impressions. The very poor developer latitude exhibited by the compositions of GB 1,245,924 makes them unsuitable for commercially acceptable lithographic printing form precursors.

[0014] Our invention utilizes a heat-sensitive composition suitable for application to a substrate, to form a heat-sensitive positive working printing form precursor for heat mode imaging which does not exhibit the disadvantages of the prior art as described hereinabove.

[0015] The composition used in the present invention is heat-sensitive in that localised heating of the composition, preferably by suitable radiation, causes an increase in the aqueous developer solubility of the exposed areas.

[0016] Therefore according to one aspect of the present invention there is provided a positive working lithographic printing form precursor having a coating comprising an oleophilic, heat-sensitive composition, the composition comprising an aqueous developer soluble polymeric substance, hereinafter called the "active polymer", and a compound which reduces the aqueous developer solubility of the polymeric substance, hereinafter called the "reversible insolubiliser compound", characterised in that the aqueous developer solubility of the composition is increased on heating and that the aqueous developer solubility of the composition is not increased by incident UV radiation.

[0017] In order to increase the sensitivity used in the heat-sensitive compositions of the present invention it is beneficial to include an additional component, namely a radiation absorbing compound capable of absorbing incident radiation and converting it to heat, hereinafter called a "radiation absorbing compound".

[0018] Therefore a further aspect of the present invention is a lithographic printing form precursor wherein said coating is suitably adapted to preferentially absorb radiation and convert said radiation to heat.

[0019] In one embodiment of the present invention there is provided a heat-sensitive positive working lithographic printing form precursor wherein the said coating includes an additional layer disposed beneath the oleophilic, heat-sensitive composition, wherein the additional layer comprises a radiation absorbing compound.

[0020] In another embodiment of the present invention there is provided a heat-sensitive positive working lithographic printing form precursor which has on a support having a hydrophilic surface and an oleophilic, heat-sensitive composition comprising a said active polymer and a said reversible insolubiliser compound which is also a said radiation absorbing compound characterised in that the aqueous developer solubility of the composition is increased on heating and that the aqueous developer solubility of the composition is not increased by incident UV radiation.

[0021] In the specification, when we state that the aqueous developer solubility of the composition is increased on heating we mean that it is substantially increased i.e., by an amount useful in a lithographic printing process. When we state that the aqueous developer solubility of the composition is not increased by incident UV radiation we mean that it is not substantially increased, that is by an amount which would mean that UV safelighting conditions would have to be employed. Thus, insubstantial increases in solubility on UV radiation may be tolerated within the scope of this invention.

[0022] The printing form is preferably a lithographic plate and will be referred to as such hereinafter.

[0023] A further aspect of the present invention relates to a method of producing a lithographic printing plate comprising direct imagewise application of heat or of heat-generating radiation to a precursor as defined herein. In such a

method a positive working lithographic printing plate is obtained after heat-mode imaging and processing. The aqueous developer solubility of the coated composition is much reduced with respect to the solubility of the active polymer alone. On subsequent exposure to suitable radiation the heated areas of the composition are rendered more soluble in the developing solution. Therefore on imagewise exposure there is a change in the solubility differential of the unexposed composition and of the exposed composition. Thus in the exposed areas the composition is dissolved revealing the underlying hydrophilic surface of the plate.

[0024] A coated plate precursor of the invention may be heat imaged indirectly by exposure to a short duration of high intensity radiation transmitted or reflected from the background areas of a graphic original located in contact with the recording material.

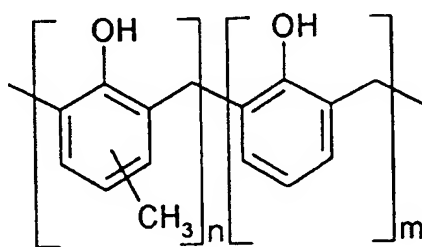
[0025] A plate precursor may be imagewise heated using a heated body. For example, the plate precursor, either the reverse face or, preferably, the heat sensitive composition, may be contacted by a heat stylus.

[0026] Preferably the plate precursor is exposed directly by means of a laser to heat the coating imagewise. Most preferably the laser emits radiation at about 600 nm.

[0027] Whilst the applicants do not wish to be limited by any theoretical explanation of how their invention operates, it is believed that a thermally frangible complex is formed between the active polymer and the reversible insolubiliser compound. This complex is believed to be reversibly formed and can be broken by application of heat to the complex to restore aqueous developer solubility to the composition. It is thought that polymeric substances suitable for use in the current invention comprise electron rich functional groups when uncomplexed and that suitable compounds which reduce the aqueous developer solubility of the polymeric substance are electron poor. It is not thought that decomposition of components within the composition is required, or that any substantial decomposition has occurred in any examples tested to date.

[0028] Examples of functional groups of said active polymers suitable for application in this invention include hydroxy, carboxylic acid, amino, amide and maleimide functional groups. A wide range of polymeric materials are suitable for use in the present invention examples of which include phenolic resins; copolymers of 4-hydroxystyrene, for example with 3-methyl-4-hydroxystyrene or 4-methoxystyrene; copolymers of (meth)acrylic acid, for example with styrene; copolymers of maleimide, for example with styrene; hydroxy or carboxy functionalised celluloses; copolymers of maleic anhydride, for example with styrene; partially hydrolysed polymers of maleic anhydride.

[0029] Most preferably the active polymer is a phenolic resin. Particularly useful phenolic resins in this invention are the condensation products from the interaction between phenol, C-alkyl substituted phenols (such as cresols and p-tert-butyl-phenol), diphenols (such as bisphenol-A) and aldehydes (such as formaldehyde). Dependent on the preparation route for the condensation a range of phenolic materials with varying structures and properties can be formed. Particularly useful in this invention are novolak resins, resole resins and novolak/resole resin mixtures. Examples of suitable novolak resins have the following general structure.



[0030] A large number of compounds which reduce the aqueous solubility of suitable polymeric substances have been located for use as reversible insolubiliser compounds.

[0031] A useful class of reversible insolubiliser compounds are nitrogen containing compounds wherein at least one nitrogen atom is either quarternised, or incorporated in a heterocyclic ring, or quarternised and incorporated in a heterocyclic ring.

[0032] Examples of useful quarternised nitrogen containing compounds are triaryl methane dyes such as Crystal Violet (CI basic violet 3) and Ethyl Violet and tetraalkyl ammonium compounds such as Cetrinide.

[0033] More preferably the reversible insolubiliser compound is a nitrogen-containing heterocyclic compound.

[0034] Examples of suitable nitrogen-containing heterocyclic compounds are quinoline and triazols, such as 1,2,4-triazol.

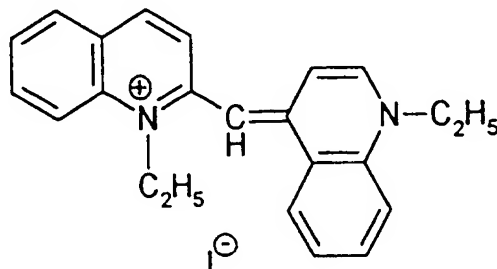
[0035] Most preferably the nitrogen-containing heterocyclic compound is a quarternised heterocyclic compound.

[0036] Examples of suitable quarternised heterocyclic compounds are imidazoline compounds, such as Monazoline

C, Monazoline O, Monazoline CY and Monazoline T all of which are manufactured by Mona Industries, quinolinium compounds, such as 1-ethyl-2-methyl quinolinium iodide and 1-ethyl-4-methyl quinolinium iodide, and benzothiazolium compounds, such as 3-ethyl-2-methyl benzothiazolium iodide, and pyridinium compounds, such as cetyl pyridinium bromide, ethyl viologen dibromide and fluoropyridinium tetrafluoroborate.

[0037] Usefully the quinolinium or benzothiazolium compounds are cationic cyanine dyes, such as Dye A, Quinoldine Blue and 3-ethyl-2-[3-(3-ethyl-2(3H)-benzothiazoylidene)-2-methyl-1-propenyl]benzothiazolium iodide.

[0038] Dye A



[0039] A further useful class of reversible insolubiliser compounds are carbonyl functional group containing compounds.

[0040] Examples of suitable carbonyl containing compounds are  $\alpha$ -naphthoflavone,  $\beta$ -naphthoflavone, 2,3-diphenyl-1-indeneone, flavone, flavanone, xanthone, benzophenone, N-(4-bromobutyl)phthalimide and phenanthrenequinone.

[0041] The reversible insolubilising compound may be a compound of general formula



Where  $Q_1$  represents an optionally substituted phenyl or alkyl group,  $n$  represents 0, 1 or 2, and  $Q_2$  represents a halogen atom or an alkoxy group. Preferably  $Q_1$  represents a  $C_{1-4}$  alkyl phenyl group, for example a tolyl group, or a  $C_{1-4}$  alkyl group. Preferably  $n$  represents 1 or, especially, 2. Preferably  $Q_2$  represents a chlorine atom or a  $C_{1-4}$  alkoxy group, especially an ethoxy group.

[0042] Another useful reversible insolubiliser compound is acridine orange base (CI solvent orange 15).

[0043] Other useful reversible insolubiliser compounds are ferrocenium compounds, such as ferrocenium hexafluorophosphate.

[0044] In addition to the active polymer which interacts with the reversible insolubiliser compound in the manner defined herein the composition may contain a polymeric substance which does not thus interact. In such a composition having a blend of polymeric substances it should be noted that the active polymer can be present in a lower amount, by weight, than the additional polymeric substance(s). Suitably the active polymer is present in an amount of at least 10%, preferably at least 25%, more preferably at least 50%, by total weight of the polymer substances present in the composition. Most preferably, however, the active polymer is present to the exclusion of any polymeric substance which does not thus interact.

[0045] The major proportion of the composition is preferably constituted by polymeric substance(s), including the active polymer and, when present, an additional polymeric substance which does not thus interact. Preferably a minor proportion of the composition is constituted by the reversible insolubiliser compound.

[0046] A major proportion as defined herein is suitably at least 50%, preferably at least 65%, most preferably at least 80%, of the total weight of the composition.

[0047] A minor proportion as defined herein is suitably less than 50%, preferably up to 20%, most preferably up to 15%, of the total weight of the composition.

[0048] Suitably the reversible insolubiliser compound constitutes at least 1%, preferably at least 2%, preferably up to 25%, more preferably up to 15% of the total weight of the composition.

[0049] Thus a preferred weight range for the reversible insolubiliser compound may be expressed as 2-15% of the total weight of the composition.

[0050] There may be more than one polymeric substance which interacts with the said compound. References herein to the proportion of such substance(s) are to their total content. Likewise there may be more than one polymeric substance which does not thus interact. References herein to the proportion of such substance(s) are to their total content. Likewise there may be more than one reversible insolubiliser compound. References herein to the proportion of such compound(s) are to their total content.

**[0051]** The aqueous developer composition is dependent on the nature of the polymeric substance. Common components of aqueous lithographic developers are surfactants, chelating agents such as salts of ethylenediamine tetraacetic acid, organic solvents such as benzyl alcohol, and alkaline components such as inorganic metasilicates, organic metasilicates, hydroxides or bicarbonates.

5 **[0052]** Preferably the aqueous developer is an alkaline developer containing inorganic or organic metasilicates when the polymeric substance is a phenolic resin.

**[0053]** Six simple tests, tests 1 to 6, may be carried out to determine if the composition comprising the active polymer and the reversible insolubiliser compound and a suitable aqueous developer are suitable for use in the present invention.

10 Test 1. The composition comprising the active polymer in the absence of the reversible insolubiliser compound is coated on a hydrophilic support and dried. Then the surface is inked-up. If a uniform inked coating is obtained then the composition is oleophilic when laid down as a layer.

15 Test 2. The hydrophilic support coated with the composition comprising the active polymer in the absence of the reversible insolubiliser compound is processed in a suitable aqueous developer for a suitable time which may be determined by trial and error but will typically be between 30 to 60 seconds, at room temperature, and then rinsed, dried and inked-up. If no ink surface is obtained then the composition has dissolved in the developer.

20 Test 3. The composition comprising the active polymer and the reversible insolubiliser compound is coated onto a hydrophilic support, dried and inked-up. If a uniform inked coating is obtained then the composition is oleophilic when laid down as a layer.

25 Test 4. The hydrophilic support coated with the composition comprising the active polymer and the reversible insolubiliser compound is processed in a suitable aqueous developer for a suitable time which may be determined by trial and error but will typically be between 30 and 60 seconds, at room temperature, and then rinsed, dried and inked-up. If a uniform inked coating is obtained then the composition does not substantially dissolve in the developing solution.

30 Test 5. The hydrophilic support coated with the composition comprising the active polymer and the reversible insolubiliser compound is heated in an oven such that the composition reaches a suitable temperature for an appropriate time. Then it is processed in a suitable aqueous developer for a reasonable period of time at room temperature.

35 The surface is then dried and inked-up. If no ink surface is obtained then the heated composition has dissolved in the developer.

40 The temperature and time depend on the components selected for the composition and on their proportion. Simple trial and error experiments may be undertaken to determine suitable conditions. If such experiments cannot yield conditions which allow the test to be passed, the conclusion must be that the composition does not pass this test.

45 Preferably, for typical compositions, the composition comprising the active polymer and the reversible insolubiliser compound is heated in an oven such that the composition reaches a temperature of 50°C to 160°C for 5 to 20 seconds. Then it is processed in a suitable aqueous developer for a suitable time which may be determined by trial and error but will typically be 30 to 120 seconds, at room temperature.

Most preferably, the composition comprising the active polymer and the reversible insolubiliser compound is heated in an oven such that the composition reaches a temperature of 50°C to 120°C for 10 to 15 seconds. Then it is processed in a suitable aqueous developer for 30 to 90 seconds at room temperature.

50 Test 6. The hydrophilic support coated with the composition comprising the active polymer and the reversible insolubiliser compound is exposed to UV light for a suitable time which may be determined by trial and error but will typically be 30 seconds. Then it is processed in a suitable aqueous developer for a suitable time which may be determined by trial and error but will typically be 30 to 60 seconds at room temperature. The surface is then dried and inked-up. If the coating is inked-up no UV radiation induced solubilisation of the composition has occurred and thus the composition is suitably robust to normal working lighting conditions.

55 **[0054]** If the composition can pass all six tests then it is suitable for use in the present invention.

**[0055]** A large number of compounds, or combinations thereof, can be utilised as radiation absorbing compounds in preferred embodiments of the present invention.

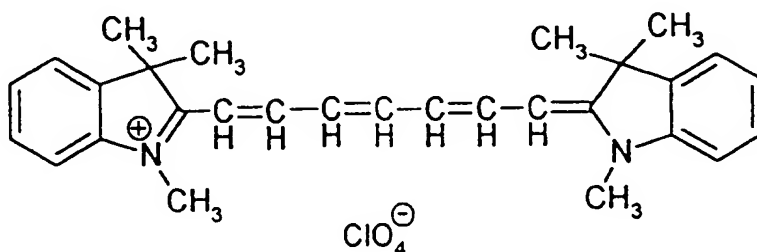
[0056] In preferred embodiments the radiation absorbing compound absorbs infra-red radiation. However, other materials which absorb other wavelength radiation (excluding UV wavelengths), e.g. 488 nm radiation from an Ar-ion laser source, may be used with the radiation being converted to heat.

[0057] The radiation absorbing compound is usefully carbon such as carbon black or graphite. It may be a commercially available pigment such as Heliogen Green as supplied by BASF or Nigrosine Base NG1 as supplied by NH Laboratories Inc or Milori Blue (C.I. Pigment Blue 27) as supplied by Aldrich.

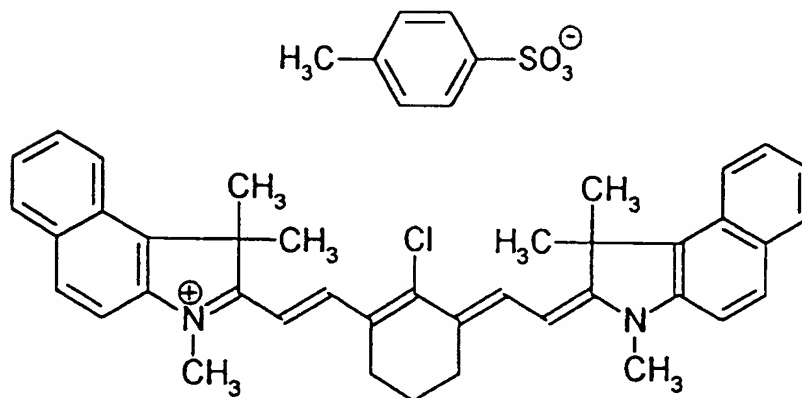
[0058] In a preferred method of the invention the coated plate is imagewise exposed directly by a laser. Most preferably the laser emits radiation at above 600 nm and the radiation absorbing compound is usefully an infra-red absorbing dye.

[0059] Preferably the infra-red absorbing compound is one whose absorption spectrum is significant at the wavelength output of the laser which is to be used in the method of the present invention. Usefully it may be an organic pigment or dye such as phthalocyanine pigment. Or it may be a dye or pigment of the squarylium, merocyanine, cyanine, indolizine, pyrylium or metal dithioline classes.

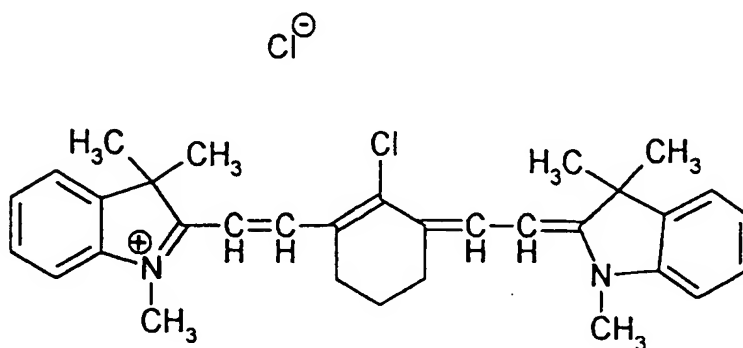
[0060] Examples of such compounds are:-



and Dye B



and Dye C, KF654 B PINA as supplied by Riedel de Haan UK, Middlesex, England, believed to have the structure:-



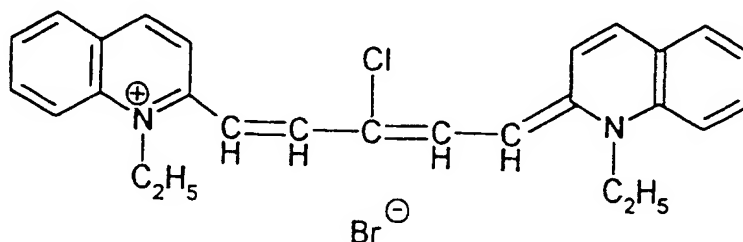
[0061] Suitably the radiation absorbing compound constitutes at least 1%, preferably at least 2%, preferably up to 25%, more preferably up to 15%, of the total weight of the composition. Thus a preferred weight range for the radiation absorbing compound may be expressed as 2-15% of the total weight of the composition. Likewise there may be more than one radiation absorbing compound. References herein to the proportion of such compound(s) are to their total content.

[0062] In one preferred embodiment of the invention an additional layer comprising a radiation absorbing compound can be used. This multiple layer construction can provide routes to high sensitivity as larger quantities of absorber can be used without affecting the function of the imaging forming layer. In principle any radiation absorbing material which absorbs sufficiently strongly in the desired wavelength range can be incorporated or fabricated in a uniform coating. Dyes, metals and pigments (including metal oxides) may be used in the form of vapour deposited layers, techniques for forming and use of such films are well known in the art, for example EP 0,652,483. The preferred components in the present invention are those that are hydrophilic as the uniform coating or which can be treated to provide a hydrophilic surface, for example by use of a hydrophilic layer.

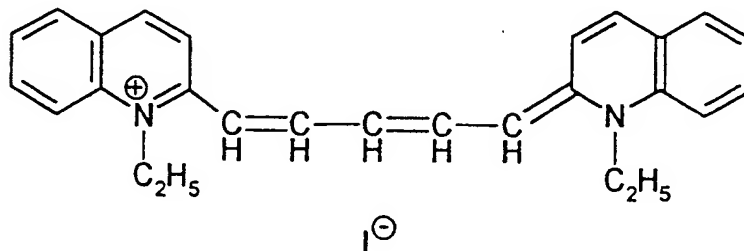
[0063] Compounds which reduce the aqueous developer solubility of the polymeric substance and are also radiation absorbing compounds suitable for one embodiment of the present invention are preferably cyanine dyes and most preferably quinolinium cyanine dyes which absorb at above 600 nm.

[0064] Examples of such compounds are:

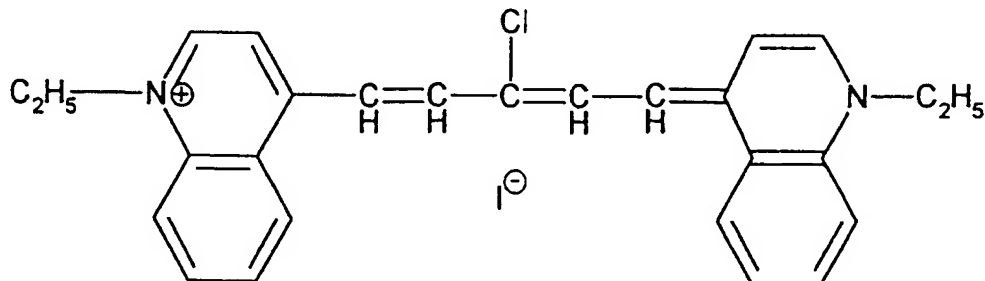
[0065] 2-[3-chloro-5-(1-ethyl-2(1H)-quinolinyldiene)-1,3-pentadienyl]-1-ethylquinolinium bromide



1-ethyl-2-[5-(1-ethyl-2(1H)-quinolinyldiene)-1,3-pentadienyl]quinolinium iodide

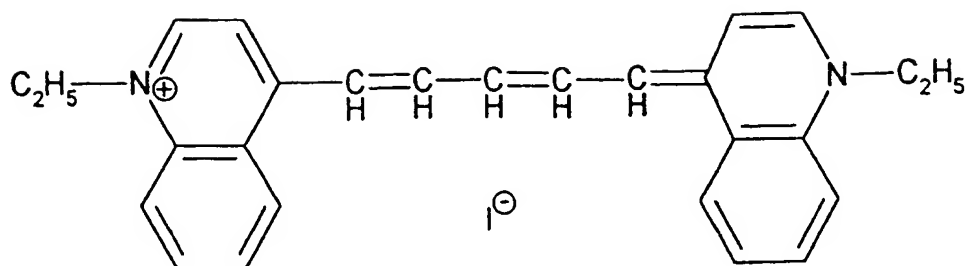


4-[3-chloro-5-(1-ethyl-4(1H)-quinolinyldiene)-1,3-pentadienyl]-ethylquinolinium iodide



Dye D, 1-ethyl-4-[5-(1-ethyl-4(1H)-quinolinyldiene)-1,3-pentadienyl]quinolinium iodide





[0066] Suitably the reversible insolubiliser compound which is also a radiation absorbing compound constitutes at least 1%, preferably at least 2%, preferably up to 25%, more preferably up to 15%, of the total weight of the composition. Thus a preferred weight range for the reversible insolubiliser compound which is also a radiation absorbing compound may be expressed as 2-15% of the total weight of the composition.

[0067] The base which can be used as the support is preferably an aluminium plate which has undergone the usual anodic, graining and post-anodic treatments well known in the lithographic art for enabling a radiation sensitive composition to be coated thereon and for the surface of the support to function as a printing background.

[0068] Another base material which may be used in the method of the present invention is a plastics material base or a treated paper base as used in the photographic industry. A particularly useful plastics material base is polyethylene terephthalate which has been subbed to render its surface hydrophilic. Also a so-called resin coated paper which has been corona discharge treated can also be used.

[0069] Examples of lasers which can be used in the method of the present invention include semiconductor diode lasers emitting at between 600 nm and 1100 nm. An example is the Nd YAG laser which emits at 1064 nm, but any laser of sufficient imaging power (whose radiation is absorbed by the composition), can be used.

[0070] The compositions of the invention may contain other ingredients such as stabilising additives, inert colourants, additional inert polymeric binders as are present in many lithographic plate compositions.

[0071] Preferably the heat-sensitive compositions of the present invention do not comprise UV sensitive components. However, UV sensitive components which are not UV activated due to the presence of other components, such as inert UV absorbing dyes or a UV absorbing topmost layer, may be present.

[0072] Any feature of any aspect of the present invention or embodiment described herein may be combined with any feature of any other aspect of any invention or embodiment described herein.

[0073] The following Examples more particularly serve to illustrate the various aspects of the present invention described hereinabove.

[0074] The following products are referred to hereinafter:-

Resin A: LB6564 - a phenol/cresol novolak resin marketed by Bakelite.

Resin B: R17620 - a phenol/formaldehyde resole resin marketed by BP Chemicals Ltd of Sully, Wales.

Resin C: SMD995 - an alkyl phenol/formaldehyde resole resin marketed by Schnectady Midland Ltd of Wolverhampton, England.

Resin D: Maruka Lyncur M(S-2) - a poly(hydroxystyrene) resin marketed by Maruzen Petrochemical Co. Ltd. of Tokyo, Japan.

Resin E: Ronacoat 300 - a polymer based on dimethylmaleimide marketed by Rohner Ltd of Pratteln, Switzerland.

Resin F: Gantrez An119 - a methylvinylether-co-maleic anhydride copolymer marketed by Gaf Chemicals Co., Guildford, England.

Resin G: SMA 2625P - a styrene maleic anhydride half ester marketed by Elf Atochem UK Ltd., Newbury, England.

Resin H: Cellulose acetate propionate (Mol. Wt. 75 000, containing 2.5% acetate and 45% to 49% propionate), marketed by Eastman Fine Chemicals, Rochester, USA.

#### Exposure test method

[0075] The coated substrate to be imaged was cut into a circle of 105 mm diameter and placed on a disc that could be rotated at a constant speed between 100 and 2500 revolutions per minute. Adjacent to the spinning disc a translating table held the source of the laser beam so that the laser beam impinged normal to the coated substrate, while the translating table moved the laser beam radially in a linear fashion with respect to the spinning disc.

[0076] The laser used was a single mode 830 nm wavelength 200 mW laser diode which was focused to a 10 micron



(continued)

	Example								
	1	2	3	4	5	6	7	8	9
Component	Parts by Weight								
Crystal violet									6
Benzothiazolium A is 3-ethyl-2-[3-ethyl-2(3H) - benzothiazolydene)-2-methyl-1-propenyl] benzothiazolium bromide. Benzothiazolium B is 3-ethyl-2-methyl benzothiazolium iodide.									

[0080] The plates were tested for developability by immersing in an aqueous developer solution for 30 seconds using an appropriate aqueous developer solution as described below.

Developer A:- 14% Sodium metasilicate pentahydrate in water.

Developer B:- 7% Sodium metasilicate pentahydrate in water.

[0081] The following table lists results of the simple developability test for the compositions.

	Developer B
Comparative example	
1 to 5	Coating totally removed
Example	
1 to 9	No significant coating removal

[0082] The compositions described in the Comparative examples do not show resistance to developer attack. The compositions described in Examples 1 to 9 illustrate the effect of reducing the polymer developer solubility through the use of compounds described in the present invention.

[0083] Further samples of the plates were then imaged using the 830 nm laser device described previously. The exposed discs were then processed by immersing in an aqueous developer solution for 30 seconds using an appropriate aqueous developer solution as described above. Plate sensitivities were then determined.

[0084] The results are listed in the following table.

	Developer A	Developer B
Comparative example		
4	No coating retained	
2	No coating retained	
3	No coating retained	
4	No coating retained	
5	No coating retained	
Example		
1		$\leq 150 \text{ mJ/cm}^2$
2	$\leq 150 \text{ mJ/cm}^2$	
3	$\leq 150 \text{ mJ/cm}^2$	
4	$\leq 150 \text{ mJ/cm}^2$	
5	$\leq 150 \text{ mJ/cm}^2$	
6	$\leq 150 \text{ mJ/cm}^2$	
7		$\leq 150 \text{ mJ/cm}^2$
8		$\leq 150 \text{ mJ/cm}^2$
9	$\leq 150 \text{ mJ/cm}^2$	

**[0085]** A printing plate made according to example 1 was also imaged on a commercially available image setter, the Trendsetter, supplied by Creo Products of Vancouver, Canada. The plate printed at least 10,000 good prints on a lithographic printing press.

#### Example 10

**[0086]** A solution containing 8.15 g 1-methoxypropan-2-ol, 2.40 g of a 40% w/w solution Resin A in 1-methoxypropan-2-ol, 0.12 g of Dye A and 0.24 g of a Carbon black dispersion at 50% (w/w) in water was prepared and coated as described in Examples 1 to 9.

Example 10	
Component	Parts by Weight
Resin A	80
Dye A	10
Carbon Black	10

**[0087]** The resulting plate was imaged using a 200m W laser diode at a wavelength of 830 nm using the imaging device described previously. The plate was then developed using Developer B for 30 seconds. The imaging energy density required to give a suitable image was  $\leq 150 \text{ mJ/cm}^2$ .

**[0088]** A printing plate made according to Example 10 was also imaged on a commercially available image setter, the Trendsetter, supplied by Creo Products of Vancouver, Canada. The plate printed at least 10,000 good prints on a lithographic printing press.

Example 11

[0089] The plate precursor with the composition described in the following table was prepared as described for Example 4.

Example 11	
Component	Parts by Weight
Resin A	90
Dye D	10

[0090] The resulting plate was imaged using a 200m W laser diode at a wavelength of 830 nm using the imaging device described previously. The plate was then developed using Developer B for 30 seconds. The imaging energy density required to give a suitable image was  $\leq 150 \text{ mJ/cm}^2$ .

[0091] A printing plate made according to Example 11 was also imaged on a commercially available image setter, the Trendsetter, supplied by Creo Products of Vancouver, Canada. The plate printed at least 10,000 good prints on a lithographic printing press.

Examples 12-18

[0092] Coating formulations were prepared as previously described as solutions in 1-methoxypropan-2-ol with the exception of Example 16 which was prepared as a solution in 1-methoxypropan-2-ol/DMF 80:20 (v:v).

[0093] The formulations were coated as described in Examples 1-9 to provide dry film compositions as described in the following table.

	Example						
	12	13	14	15	16	17	18
Component	Parts by Weight						
Crystal Violet	6	6	6	6	6	6	6
Dye C	4	4	4	4	4	4	4
Resin A		45					
Resin B	90						
Resin C		45					
Resin D			90				
Resin E				90			
Resin F					90		
Resin G						90	
Resin H							90

[0094] Samples of the plates were then imaged using the 830 nm laser device described previously. The exposed discs were then processed by immersing in a suitable aqueous developer solution, as described previously and below, for an appropriate time. Plate sensitivities were then determined. The results are listed in the following table.

Developer C: 15%  $\beta$ -naphthylethoxylate, 5% benzyl alcohol, 2% nitrilo-triacetic acid trisodium salt, 78% water.

Developer D: 3%  $\beta$ -naphthylethoxylate, 1% benzyl alcohol, 2% nitrilo-triacetic acid trisodium salt, 94% water.

Developer E: 1.5%  $\beta$ -naphthylethoxylate, 0.5% benzyl alcohol, 1% nitrilo-triacetic acid trisodium salt, 97% water.

	Developer	Time/seconds	Sensitivity
Example			
12	B	90	248 mJ/cm <sup>2</sup>
13	A	60	277 mJ/cm <sup>2</sup>
14	C	45	277 mJ/cm <sup>2</sup>
15	D	5	253 mJ/cm <sup>2</sup>
16	E	60	461 mJ/cm <sup>2</sup>
17	D	60	300 mJ/cm <sup>2</sup>
18	A	120	700 mJ/cm <sup>2</sup>

#### Examples 19-30

[0095] Coating formulations were prepared as previously described as solutions in 1-methoxypropan-2-ol with the exception of example 26 which was prepared as a solution in 1-methoxypropan-2-ol/DMF 50:50 (v:v).

[0096] The formulations were coated as described in Examples 1-9 to provide dry film compositions as described in the following table.

	Example												
	19	20	21	22	23	24	25	26	27	28	29	30	
Component	Parts by Weight												
Dye B	4	4	4	4	4	4	4	4					
Dye C									4	4	4	4	
Resin A	90	90	90	90	90	90	90	90	90	90	90	90	
$\alpha$ -Naphthoflavone	6												
$\beta$ -Naphthoflavone		6											
Flavone			6										
Xanthone				6									
Flavanone					6								
Benzophenone						6							
2,3-Diphenyl-1-indeneone							6						
N-(4-bromobutyl) phthalimide								6					
Phenanthrene quinone									6				
Acridine Orange Base (CI solvent orange 15)										6			
p-Toluene sulfonyl chloride											6		
Ethyl-p-toluene sulfonate												6	

[0097] Samples of the plates were then imaged using the 830 nm laser device described previously. The exposed discs were then processed by immersing in a suitable aqueous developer solution for an appropriate time. Plate sensi-

tivities were then determined. The results are listed in the following table.

	Developer	Time/seconds	Sensitivity
Example			
19	A	30	$\leq 150 \text{ mJ/cm}^2$
20	A	30	$\leq 150 \text{ mJ/cm}^2$
21	A	30	$290 \text{ mJ/cm}^2$
22	A	30	$\leq 150 \text{ mJ/cm}^2$
23	A	30	$\leq 150 \text{ mJ/cm}^2$
24	B	30	$220 \text{ mJ/cm}^2$
25	B	30	$\leq 150 \text{ mJ/cm}^2$
26	B	15	$\leq 150 \text{ mJ/cm}^2$
27	B	60	$250 \text{ mJ/cm}^2$
28	A	90	$250 \text{ mJ/cm}^2$
29	B	10	$400 \text{ mJ/cm}^2$
30	B	60	$250 \text{ mJ/cm}^2$

#### Example 31

[0098] The coating formulation was prepared as previously described as a solution in 1-methoxypropan-2-ol. The formulation was coated as described in Examples 1-9 to provide a dry film composition as described in the following table.

Example 31	
Component	Parts by Weight
Resin A	90
Dye C	4
Crystal Violet	6

[0099] Samples of the plate were subjected to heat delivered from a Weller Soldering Iron EC 2100 M at 311°C. The speed of movement of the soldering iron over the plate surface is described in the table below. The exposed plate samples were then processed by immersion in developer A for 60 seconds. The results are listed in the table below.

Speed of Soldering Iron Movement over Plate Surface ( $\text{cm s}^{-1}$ )	Heat applied to...	Simple Developability Test Result
1	coated face of plate	Coating totally removed in area subjected to heat
10	coated face of plate	Coating totally removed in area subjected to heat

(continued)

Speed of Soldering Iron Movement over Plate Surface (cm s <sup>-1</sup> )	Heat applied to...	Simple Developability Test Result
20	coated face of plate	Coating totally removed in area subjected to heat
50	coated face of plate	Coating totally removed in area subjected to heat
1	reverse face of plate, ie direct on the aluminium support	Coating totally removed in area subjected to heat
10	reverse face of plate, ie direct on the aluminium support	Coating totally removed in area subjected to heat

[0100] In the specification, we refer in various places to UV light. A person skilled in the art will be aware of the typical wavelength range of UV light. However, for the avoidance of any doubt, UV typically has a wavelength range of 190 nm to 400 nm.

[0101] All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive.

#### Claims

1. A positive working lithographic printing form precursor having a coating comprising an oleophilic, heat-sensitive composition, the composition comprising an aqueous developer soluble polymeric substance, and a compound which reduces the aqueous developer solubility of the polymeric substance characterised in that the aqueous developer solubility of the composition is increased on heating and that the aqueous developer solubility of the composition is not increased by incident UV radiation.
2. A precursor as claimed in claim 1 wherein the aqueous developer soluble polymeric substance is a phenolic resin.
3. A precursor as claimed in claim 1 or 2 wherein the compound which reduces the aqueous developer solubility of the polymeric substance is selected from a imidazoline compound, a quinolinium compound, a benzothiazolium compound and a pyridinium compound.
4. A precursor as claimed in claim 1, 2 or 3 wherein the compound which reduces the aqueous developer solubility of the polymeric substance is a cyanine dye.
5. A precursor as claimed in claims 3 and 4 wherein the quinolinium compound is a cyanine dye.
6. A precursor as claimed in any preceding claim wherein said coating is adapted to preferentially absorb and convert said radiation to heat.
7. A precursor as claimed in claim 6 wherein said composition comprises a radiation absorbing compound capable of absorbing incident radiation and converting it to heat.
8. A precursor as claimed in claim 7 wherein the radiation absorbing compound is carbon black.
9. A precursor as claimed in claim 7 wherein the radiation absorbing compound is a pigment.
10. A precursor as claimed in claim 9 wherein the pigment is an organic pigment.
11. A precursor as claimed in claim 10 wherein the pigment is a phthalocyanine pigment.
12. A precursor as claimed in claim 7 wherein the radiation absorbing compound is a dye selected from one of the following classes, squarylium, merocyanine, indolizine, pyrylium or metal dithioline.



13. A precursor as claimed in claim 7 wherein the compound which reduces the aqueous developer solubility of the polymeric substance is also a radiation absorbing compound capable of absorbing incident radiation and converting it to heat, said compound being a cyanine dye which comprises a quinolinium moiety.
- 5 14. A precursor as claimed in any of claims 7 to 13 wherein the radiation absorbing compound absorbs at above 600 nm.
15. A method for producing a lithographic printing form comprising direct imagewise application of heat or of heat-generating radiation to a precursor as claimed in any preceding claim.
- 10 16. A method as claimed in claim 15 wherein heat-generating radiation is delivered from a laser.
17. A method as claimed in claim 16 wherein the laser emits radiation at above 600 nm.
- 15 18. A method as claimed in claim 15 wherein heat is delivered from a heated body.
19. A method as claimed in any of claims 15 to 18, wherein the aqueous developer solution is an aqueous alkaline solution.
- 20 20. An imaged printing form produced by application of a method as claimed in any of claims 15 to 19 to a lithographic printing form precursor as claimed in any of claims 1 to 14.

### Patentansprüche

- 25 1. Vorläufer einer positiv arbeitenden Lithographie-Druckform mit einer Beschichtung, umfassend eine oleophile, wärmeempfindliche Zusammensetzung, wobei die Zusammensetzung eine in wäßrigem Entwickler lösliche polymere Substanz und eine Verbindung, welche die Löslichkeit der polymeren Substanz in wäßrigem Entwickler verringert, umfaßt, dadurch gekennzeichnet, daß die Löslichkeit der Zusammensetzung in wäßrigem Entwickler durch Erwärmen erhöht und die Löslichkeit der Zusammensetzung in wäßrigem Entwickler durch einfallende UV-Strahlung
- 30 nicht erhöht wird.
2. Vorläufer nach Anspruch 1, wobei die in wäßrigem Entwickler lösliche polymere Substanz ein Phenolharz ist.
3. Vorläufer nach Anspruch 1 oder 2, wobei die Verbindung, welche die Löslichkeit der polymeren Substanz in wäßrigem Entwickler verringert, ausgewählt ist aus einer Imidazolinverbindung, einer Chinoliniumverbindung, einer Benzothiazoliumverbindung und einer Pyridiniumverbindung.
- 35 4. Vorläufer nach Anspruch 1, 2 oder 3, wobei die Verbindung, welche die Löslichkeit der polymeren Substanz in wäßrigem Entwickler verringert, ein Cyaninfarbstoff ist.
- 40 5. Vorläufer nach Anspruch 3 oder 4, wobei die Chinoliniumverbindung ein Cyaninfarbstoff ist.
6. Vorläufer nach einem der vorstehenden Ansprüche, wobei die Beschichtung hergerichtet ist, um vorzugsweise Strahlung zu absorbieren und in Wärme umzuwandeln.
- 45 7. Vorläufer nach Anspruch 6, wobei die Zusammensetzung eine strahlungsabsorbierende Verbindung enthält, die einfallende Strahlung absorbieren und sie in Wärme umwandeln kann.
8. Vorläufer nach Anspruch 7, wobei die strahlungsabsorbierende Verbindung Ruß ist.
- 50 9. Vorläufer nach Anspruch 7, wobei die strahlungsabsorbierende Verbindung ein Pigment ist.
10. Vorläufer nach Anspruch 9, wobei das Pigment ein organisches Pigment ist.
- 55 11. Vorläufer nach Anspruch 10, wobei das Pigment ein Phthalocyaninpigment ist.
12. Vorläufer nach Anspruch 7, wobei die strahlungsabsorbierende Verbindung ein Farbstoff ist, ausgewählt aus der Squarylium-, Merocyanin-, Indolizin-, Pyrylium- oder Metall-Dithiolin-Klasse.

13. Vorläufer nach Anspruch 7, wobei die Verbindung, welche die Löslichkeit der polymeren Substanz in wäßrigem Entwickler verringert und welche ebenfalls eine strahlungsabsorbierende Verbindung, die einfallende Strahlung absorbieren und in Wärme umwandeln kann, ist, ein Cyaninfarbstoff ist, der eine Chinoliniumeinheit umfaßt.
- 5 14. Vorläufer nach einem der Ansprüche 7 bis 13, wobei die strahlungsabsorbierende Verbindung oberhalb 600 nm absorbiert.
15. Verfahren zur Herstellung einer Lithographie-Druckform, umfassend die direkte bildweise Applikation von Wärme oder wärmeerzeugender Strahlung auf einen in einem der vorstehenden Ansprüche beschriebenen Vorläufer.
- 10 16. Verfahren nach Anspruch 15, bei welchem die wärmeerzeugende Strahlung von einem Laser abgegeben wird.
17. Verfahren nach Anspruch 16, bei welchem der Laser Strahlung oberhalb 600 nm aussendet.
- 15 18. Verfahren nach Anspruch 15, bei welchem die Wärme von einem beheizten Körper abgegeben wird.
19. Verfahren nach einem der Ansprüche 15 bis 18, wobei die Lösung des wäßrigen Entwicklers eine wäßrige alkalische Lösung ist.
- 20 20. Bebilderte Druckform, die durch Anwendung eines Verfahrens nach einem der Ansprüche 15 bis 19 auf einen Druckformvorläufer nach einem der Ansprüche 1 bis 14 hergestellt wird.

#### Revendications

- 25 1. Précurseur de cliché lithographique fonctionnant en positif ayant un revêtement comprenant une composition thermosensible oléophile, la composition comprenant une substance polymère soluble dans un révélateur aqueux et un composé qui réduit la solubilité de la substance polymère dans un révélateur aqueux, caractérisé en ce que la solubilité dans un révélateur aqueux de la composition est augmentée lors du chauffage et en ce que la solubilité dans un révélateur aqueux de la composition n'est pas augmentée par un rayonnement UV incident.
- 30 2. Précurseur selon la revendication 1, dans lequel la substance polymère soluble dans un révélateur aqueux est une résine phénolique.
- 35 3. Précurseur selon la revendication 1 ou 2, dans lequel le composé qui réduit la solubilité dans un révélateur aqueux de la substance polymère est choisi parmi un composé d'imidazoline, un composé de quinolinium, un composé de benzothiazolium et un composé de pyridinium.
- 40 4. Précurseur selon la revendication 1, 2 ou 3, dans lequel le composé qui réduit la solubilité dans un révélateur aqueux de la substance polymère est un colorant de cyanine.
- 45 5. Précurseur selon les revendications 3 et 4, dans lequel le composé de quinolinium est un colorant de cyanine.
6. Précurseur selon l'une quelconque des revendications précédentes, dans lequel ledit revêtement est adapté pour préférentiellement absorber et convertir ledit rayonnement en chaleur.
7. Précurseur selon la revendication 6, dans lequel ladite composition comprend un composé absorbant un rayonnement, capable d'absorber un rayonnement incident et de le convertir en chaleur.
- 50 8. Précurseur selon la revendication 7, dans lequel le composé absorbant un rayonnement est le noir de carbone.
9. Précurseur selon la revendication 7, dans lequel le composé absorbant un rayonnement est un pigment.
10. Précurseur selon la revendication 9, dans lequel le pigment est un pigment organique.
- 55 11. Précurseur selon la revendication 10, dans lequel le pigment est un pigment de phtalocyanine.
12. Précurseur selon la revendication 7, dans lequel le composé absorbant un rayonnement est un colorant choisi parmi l'une des classes suivantes : squarylium, mérocyanine, indolizine, pyrylium et dithioline métallique.

13. Précurseur selon la revendication 7, dans lequel le composé qui réduit la solubilité dans un révélateur aqueux de la substance polymère est aussi un composé absorbant un rayonnement capable d'absorber un rayonnement incident et de le convertir en chaleur, ledit composé étant un colorant de cyanine qui comprend un fragment quinolinium.

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14. Précurseur selon l'une quelconque des revendications 7 à 13, dans lequel le composé absorbant un rayonnement absorbe au-delà de 600 nm.

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15. Procédé pour produire un cliché lithographique, comprenant l'application directe sous forme d'image de chaleur ou d'un rayonnement générateur de chaleur sur un précurseur selon l'une quelconque des revendications précédentes.

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16. Procédé selon la revendication 15, dans lequel le rayonnement générateur de chaleur est produit à partir d'un laser.

17. Procédé selon la revendication 15, dans lequel le laser émet un rayonnement à plus de 600 nm.

18. Procédé selon la revendication 15, dans lequel la chaleur est produite à partir d'un corps chauffé.

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19. Précurseur selon l'une quelconque des revendications 15 à 18, dans lequel la solution aqueuse de révélateur est une solution aqueuse alcaline.

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20. Cliché d'image produit par mise en oeuvre d'un procédé selon l'une quelconque des revendications 15 à 19 sur un précurseur de cliché lithographique selon l'une quelconque des revendications 1 à 14.

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